



## Electrochemically prepared acrylamide/*N,N'*-methylene bisacrylamide gels

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### Abstract

Acrylamide/*N,N'*-methylene bisacrylamide gels were synthesized electrochemically at room temperature in the presence of an initiator only, without using chemical activator. Various electrode systems were examined and silver was chosen as a working electrode material. Working conditions were determined and the effect of bisacrylamide concentration and electrode voltage on gelation times was examined.

### 1. Introduction

Polyacrylamide gels have diverse applications. Their ability to absorb solvents 50 to 100 times more than their original weight and retain their durability enhances their use, especially in hydrolysed form in holding aqueous solutions. They are used extensively as sieving systems in column chromatography and electrophoresis in analytical separation processes. They also have biomedical applications in artificial organs, contact lenses and controlled drug release systems both for human and animal therapy [1].

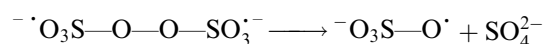
The acrylamide/*N,N'*-methylene bisacrylamide (bisacrylamide) reaction is a free radical crosslinking copolymerization. The formation and properties of polyacrylamide gels and the gelation processes have been extensively studied [2–8]. In acrylamide gelation, it is usual to use an initiator and an activator in addition to the monomers.

Gel applications, especially in biomedical systems, require very clean gels. For this reason electrochemical gelation was performed to avoid the chemical activator. The electrochemical method for initiating polymerization is very simple to operate and can be performed at room temperature.

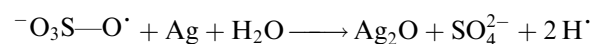
Electrolysis of acrylamide solutions is known to produce two products; polyacrylamide dissociates on the anode and soluble Nylon 3 is produced on the cathode [9]. Tashiro and coworkers have investigated the initiation of the 4-vinylpyridine (4-VP) polymerization by a free radical mechanism using a silver cathode [10]. Electropolymerization of acrylamide/bisacrylamide in forming cross linked polymer films in the presence of  $\text{ZnCl}_2$  was reported by Collins and Thomas [11]. In their experiment a crosslinking reaction occurred on the metal cathode surface and according to the author's

knowledge there is no electrochemically prepared acrylamide gel in the bulk.

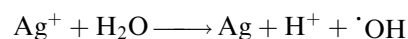
The gelation was initiated by the persulphate dissociation on the silver electrode surface as follows [12, 13]:



The radical then attacks the silver electrode.

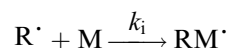
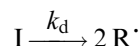


Oxidized silver is soluble in water.

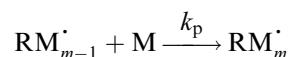
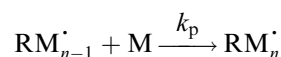
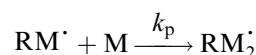


Radicals form in all these three reactions and initiate free radical polymerization of the acrylamide/bisacrylamide system as follows:

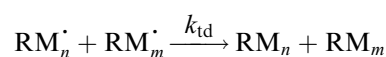
Initiation

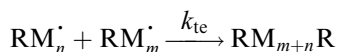


Propagation

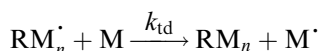


Termination

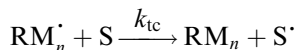




Transfer to monomer



Transfer to substrate



End group studies have shown both sulphate and hydroxide groups at the ends of the polymer chains [13]. In the present work the gel formation started on the silver electrode and extended into the cell at room temperature (20 °C). As the reaction proceeded the gel filled the whole cell.

## 2. Experimental details

Electrochemical experiments were carried out using a Wenking HP 88 high power potentiostat, a Tacussel GSTP 4 signal generator and a BBC Metrawatt X-Y recorder. Electrolyte solutions were prepared from ultrapure water (Millipore Milli Q system). All experiments were performed in a classical three electrode cell with a platinum wire as counter electrode and a calomel electrode as reference. The working electrode was a silver wire with a geometric surface of 1.5 cm<sup>2</sup>.

The optical clarities of gels having different bis concentrations were obtained in the 300–900 nm range using a Perkin Elmer Lambda 2 UV-VIS spectrophotometer.

After removing the residual monomer in the gels, chemically and electrochemically prepared gels were dried and powdered and FTIR spectra were obtained in solid form (ATI Unicam Mattson 1000 spectrophotometer).

Acrylamide (Sigma) was used after recrystallization. Bisacrylamide (Sigma), ammonium persulphate (Merck) and potassium sulphate (Merck) were used as supplied.

The gels were prepared using 50 ml solution of 0.62 M acrylamide, 0.09 M bisacrylamide and 0.005 M ammonium persulphate. The solution was deoxygenated by nitrogen bubbling for 15 min prior to the experiments. In all voltammetric experiments the solution was stirred continuously using a magnetic stirrer at constant speed. Gelation times were determined visually from the motion of a magnetic stirrer in the electrochemical cell. The gel point was defined to be the time at which a slowing down of the magnet was first seen.

To verify that the reaction is electrochemical an identical mixture of the monomer and the initiator was prepared and kept at the same temperature (20 °C). No polymerization occurred in this mixture over 24 h.

Swelling experiments were continued up to five months, changing the water every five days.

## 3. Results and discussion

Synthesis of acrylamide/bisacrylamide gels was attempted at potential controlled conditions using platinum, gold, nickel and silver electrodes under the same conditions. Gelation occurred only in the case of silver.

The electrocatalytic behaviour of silver electrode was investigated in different solutions by cyclic voltammetry. The voltammogram of the silver electrode in support electrolyte (0.1 M K<sub>2</sub>SO<sub>4</sub>) is shown in Figure 1. Desorption and adsorption of water residues was observed. Figure 1 shows that during the positive-going sweep the oxidation of silver begins at 0.35 V vs SCE. No well defined peak corresponding to the oxidation of the silver surface is observed until oxygen evolution at 0.8 V. In a neutral solution during anodic polarization of silver Ag<sub>2</sub>O is initially produced up to the establishment of the Ag/Ag<sub>2</sub>O equilibrium [12]. During the negative going-sweep from 0.8 to 0.35 V a positive current is observed. At this point the surface begins to be reduced and a negative current is observed at lower voltages.

The cyclic voltammogram of the Ag electrode in 0.1 M ammonium persulphate is shown in Figure 2. During the positive going-sweep, oxidation begins at 0.3 V vs SCE giving a step rise at 0.6 V. This step is due to the

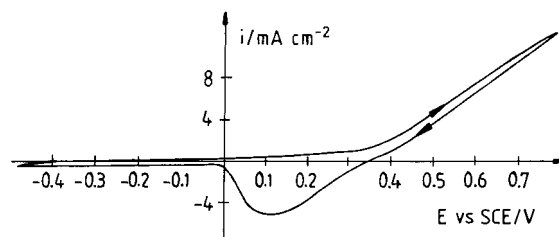


Fig. 1. Cyclic voltammogram of Ag electrode in 0.1 M K<sub>2</sub>SO<sub>4</sub>. (Sweep rate,  $\nu = 50 \text{ mV s}^{-1}$ ).

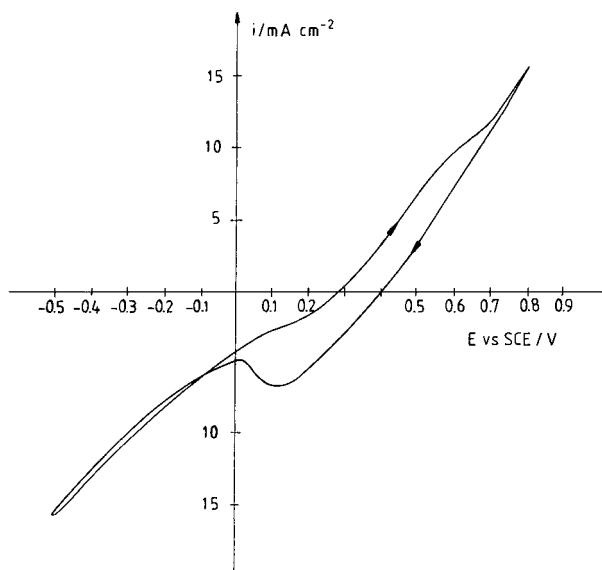


Fig. 2. Cyclic voltammogram of Ag electrode in 0.1 M (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. (Sweep rate,  $\nu = 50 \text{ mV s}^{-1}$ ).

formation of  $\text{Ag}_2\text{O}$  and  $\text{AgO}$ . The presence of this powerful oxidizing agent (persulphate) oxidizes the Ag (pH  $\sim 4$ ).  $\text{AgO}$  and  $\text{Ag}_2\text{O}$  dissolved in the water and the electrode was not passified. After dissolution these oxides are unstable and decompose water with the formation of hydroxide radicals [12]. Oxygen evolution is observed beyond 0.8 V. During the negative-going sweep a positive current occurs up to 0.4 V. This corresponds to the dissolution of oxides. The reduction of the silver surface gives a maximum in the negative current at 0.1 V, a negative current observed from 0 V to  $-0.5$  V may be due to the reduction of persulphate.

The first cycle after the addition of the acrylamide/bisacrylamide to the persulphate is given in Figure 3. The oxidation begins at 0.35 V and continues up to 0.8 V. After repeating the cycle for 30 min, the cyclic voltammogram of Figure 4 is obtained. The asymmetry of the voltammogram indicates the irreversible nature of gelation. The current density at 0.8 V also drops from about  $0.9 \text{ mA cm}^{-2}$  (in Figure 3) to  $0.7 \text{ mA cm}^{-2}$  (in Figure 4) due to increasing viscosity and the resulting decrease in ion mobility as the medium evolves from solution to gel state.

As seen in Figure 3, the oxidation starts at about 0.3 V and the 0.3–0.8 V range is found to be effective for gelation. Gel is also formed at any constant voltage within the specified range.

We have investigated the effect of potential on gel formation varying the potential between 0.35 and 0.6 V. With increasing potential, gelation time decreases. Figure 5 shows the variation of gelation time as a function of working voltage. No effect of bisacrylamide concentration is observed on the gelation time.

In Figure 6, the conversion time plot for the gelation reaction at 0.5 V is given. There is a rather long

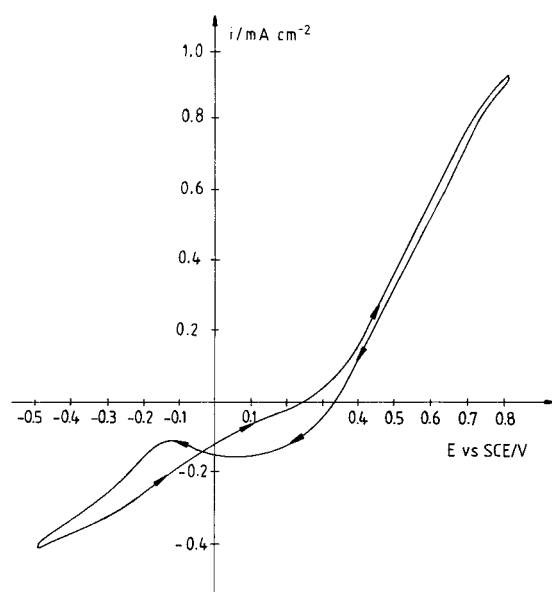


Fig. 3. First cycle of Ag electrode voltammogram in  $0.005 \text{ M } (\text{NH}_4)_2\text{S}_2\text{O}_8$  with  $0.62 \text{ M}$  acrylamide and  $0.09 \text{ M}$   $N,N'$ -methylenebisacrylamide. (Sweep rate,  $\nu = 50 \text{ mV s}^{-1}$ ).

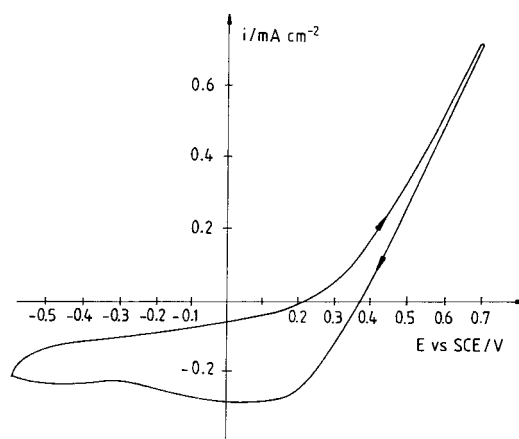


Fig. 4. Voltammogram taken after 30 min cycling as in the same conditions of Fig. 3.

induction period ( $\sim 10$  min) compared to the time to reach the full conversion. Due to the low monomer concentration of the medium (4%), the Tromsdorf Norrish effect (the gel effect) was not met during the reaction. The gelation times determined visually from the movements of the stirring magnet (Figure 5) correspond to very high conversion values. These gelation times are probably overestimates because the gel structure is too weak to effect the motion of the magnet just after the gel point. However, the same overestimates apply for reactions at all voltages and the tendency of decreasing gelation time with increasing voltage is valid.

In Figure 7 FTIR spectra of chemically and electrochemically prepared gels are given. Both have the same well-defined peaks which indicates the same structure of chemically and electrochemically prepared gels.

Optical clarities of freshly prepared gels were measured spectrophotometrically using a UV–VIS spectrometer at 300–900 nm. The transmittance of gels prepared at 0.5 V with different crosslinker concentrations are given in Figure 8. The gels with  $0.045 \text{ M}$  and  $0.09 \text{ M}$  bisacrylamide contents are clear and the opacity increased with bisacrylamide content beyond  $0.09 \text{ M}$ . The gels with lower bisacrylamide contents were soft

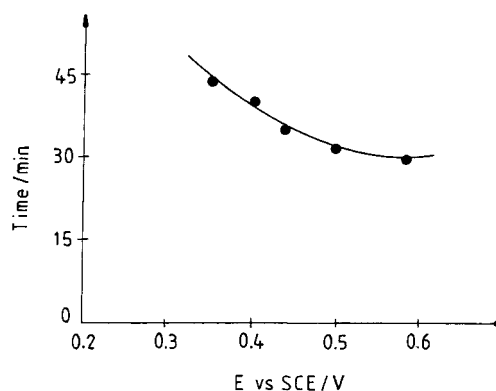


Fig. 5. The variation of gelation times versus gelation potentials in the presence of  $0.005 \text{ M } (\text{NH}_4)_2\text{S}_2\text{O}_8$ ,  $0.62 \text{ M}$  acrylamide and  $0.09 \text{ M}$  methylene bisacrylamide.

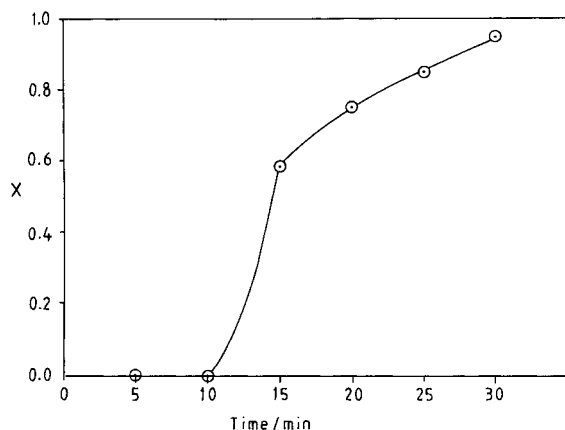


Fig. 6. Conversion against time plot of gelation reaction (0.09 M bisacrylamide, 0.62 M acrylamide and 0.005 M  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) at 0.5 V vs SCE.

and elastic but those with higher bisacrylamide content were hard and brittle. Even though they were in a swollen state the gels with higher bisacrylamide contents were easily broken into pieces.

Gelation is complete at the end of the reaction and no water is excluded. At equilibrium, the swelling by a good solvent is given by [8, 14]

$$v = \frac{1}{M_c} = \frac{V_p + \chi V_p + \ln(1 - V_p)}{d_p V_o (V_p^{1/3} - V_p/2)} \quad (1)$$

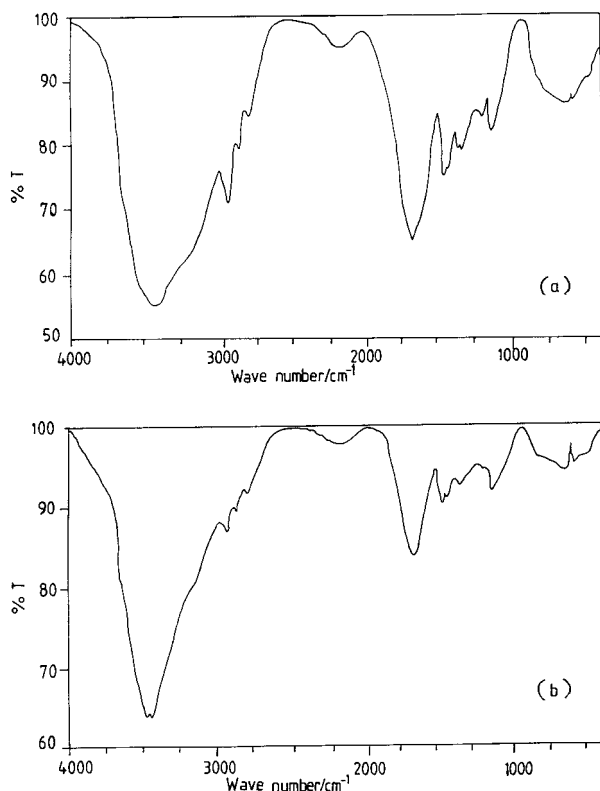


Fig. 7. FTIR spectra of the acrylamide/bisacrylamide for (a) electrochemically prepared gel and (b) chemically prepared gel.

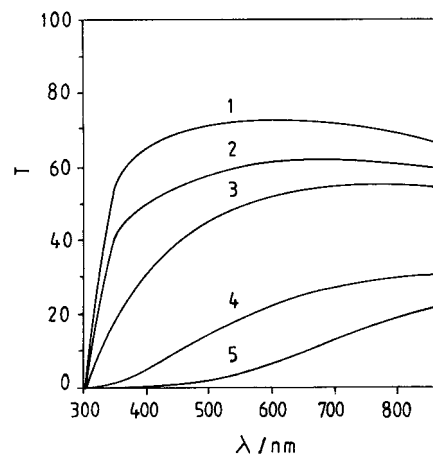


Fig. 8. UV-VIS spectra of the electrochemically prepared acrylamide/bisacrylamide gels with different bisacrylamide contents (1: 0.045 M, 2: 0.09 M, 3: 0.18 M, 4: 0.27 M, 5: 0.36 M). Transmittance values are given in arbitrary units.

where  $v$  is the effective number of moles of crosslinked chains per gram of polymer,  $M_c$  is the molecular weight between cross links,  $V_p$  is the volume fraction of polymer in the swollen mass,  $V_o$  is the molar volume of the solvent,  $\chi$  is the polymer-solvent interaction parameter,  $d_p$  is the density of the polymer and  $d_w$  is the density of water. The volume fraction of the polymer in a swollen mass can be calculated by Equations (2) and (3):

$$V_p = \frac{1}{1 + Q} \quad (2)$$

$$Q = \frac{\text{wt. of solvent in gel}}{\text{wt. of gel}} \left( \frac{d_p}{d_w} \right) \quad (3)$$

Using the experimental data together with  $d_p = 1.35 \text{ g ml}^{-1}$ ,  $d_w = 1 \text{ g ml}^{-1}$ ,  $V_o = 18 \text{ ml mol}^{-1}$ ,  $\chi = 0.48$  and  $V_p = 0.019$ ,  $M_c$  is found as 600 000, for the 1.23% bisacrylamide content in our reaction.

The swelling ratio was found (weight of swollen gel/weight of dry gel) to be 40.33 by weight. The  $M_c$  value is extremely high when compared with Okay's result which was 120 000. Our swelling ratio and bis content are very low. The effective number of mols per gram of polymer is extremely low ( $1.7 \times 10^{-6}$ ) in our case. This means either only a small portion of the crosslinker is used, or cyclization is very high in electrogelation.

In this work the gelation of acrylamide/bisacrylamide solution was initiated at the silver electrode surface and the gel filled the reaction medium soon after the start of the reaction. Further studies are needed to study the kinetics of electrochemical gelation and the properties of electrochemically formed gels.

#### Acknowledgement

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## References

1. W.M. Thomas and D.W. Wang, 'Encyclopedia of Polymer Science and Engineering' Vol.1 (Interscience, J. Wiley & Sons, New York, 1991), p. 169.
2. J. Baselga, M.A. Llorente, I. Hernandez-Fuentes and I.F. Pierola, *Eur. Polym. J.* **24** (1988) 161.
3. J. Baselga, M.A. Llorente, I. Hernandez-Fuentes and I.F. Pierola, *Eur. Polym. J.* **25** (1989) 471.
4. J. Baselga, M.A. Llorente, I. Hernandez-Fuentes and I.F. Pierola, *Eur. Polym. J.* **24** (1989) 477.
5. H. Tobita and A.E. Hamielec, *Polymer* **31** (1990) 1546.
6. I. Capek and W. Funke, *Makromol Chem.* **191** (1990) 121.
7. O. Okay, H.J. Nagash and I. Capek, *Polymer* **12** (1995) 2413.
8. H.J. Nagash and O. Okay, *J. Appl. Polym. Sci.* **60** (1996) 971.
9. S.N. Bahadani, Y.K. Prasad and S. Kundu, *J. Polym. Sci. Polym. Chem. Ed.* **18** (1980) 1459.
10. K. Tashiro, K. Marsushima and M. Kabayashi, *J. Phys. Chem.* **94** (1990) 3197.
11. G.L. Collins and N.W. Thomas, *J. Polym. Sci.* **15** (1977) 1819.
12. M. Pourbaix, 'Atlas of Electrochemical Equilibria', (Pergamon, London, 1966), p. 394.
13. C.H. Bamford, 'Encyclopedia of Polymer Science and Engineering' (Interscience, J. Wiley & Sons, New York), **13** (1991), pp. 708–867.
14. S.S. Labana, 'Encyclopedia of Polymer Science and Engineering' (Interscience, J. Wiley & Sons, New York), **4** (1991), pp. 350–395.